

# Shear and Thermal History Effects in Polypropylene Melts

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## Synopsis

Fiber grade polypropylenes with melt flow indices of 3 and 12 were studied in the as-polymerized (powder) state and after pelletization. Pelletizing operations caused very little change in the molecular weight distributions of these polymers. The lower melt flow index material exhibited much greater apparent viscosity and melt elasticity in the powder than in the pellet form during screw extrusion at 190°C. These results are consistent with the existence of a higher entanglement density in the powder version. Instron rheometer data showed no difference between the two polymer forms because of the possibility for entanglement in the rheometer reservoir during rheological experiments. The effects of sample history noted with the 3 melt flow polymer were less pronounced with the lower molecular weight 12 melt flow material. The differences in flow curves of powder and pelletized forms of the latter polymer were negligible at 175 and 190°C. Differences in die swell were more noticeable, however. The effects observed are attributable to reversible shear-induced decreases in entanglement density. Similar phenomena have been reported for other polymers. The results reported here have implications in quality control procedures for thermoplastics and in the production of polymers with desired property balances.

## INTRODUCTION

The shear and thermal history of a polymer melt may affect its subsequent processing behavior.<sup>1</sup> In general, if the melt is sheared mechanically so as to effect a disentanglement of molecules the material can be processed in a transient less elastic, and possibly less viscous, state. This will occur if recovery of an equilibrium, more fully entangled state is not rapid compared to the time scale of the subsequent melt processing operation. A relatively disentangled polymer can be restored to a more highly elastic state by annealing in the melt.<sup>2-4</sup>

Most current literature on this subject has been concerned with polyethylene, and particularly with the high pressure, low density product.<sup>4-7</sup> Linear low density polyethylene,<sup>2</sup> acetal polymers,<sup>8</sup> plasticized poly(vinyl chloride),<sup>9</sup> and Polyisobutylene<sup>10</sup> have also been reported to exhibit effects consistent with property changes involving shear-induced decreases in entanglement density.

The only publication we have been able to locate on polypropylene describes various melt elasticity effects which are influenced by sample prep-

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aration history.<sup>11</sup> It was of interest, therefore, to determine whether the phenomena mentioned are of significance in commercial grades of this polymer.

It is well known, of course, that the properties of a polymer depend on its constitution and molecular weight distribution. The reasoning outlined above suggests that the polymer characteristics may be influenced also by its shear and thermal history after polymerization. It would be expected as well, that such post-polymerization effects would be more pronounced in higher molecular weight species where the attainable entanglement densities may be higher. It was of interest, then, to compare the melt processing behavior of polypropylenes, as polymerized and after pelletization. Two propylene homopolymers with different molecular weights and melt flow indices were compared in this study.

We have also used the occasion to examine melt flow characterization procedures, using a small, single screw extruder and a capillary extrusion rheometer. Operation of the rheometer normally provides some opportunity for annealing of polymer melts during warm-up and residence in the instrument's reservoir. The screw extruder, on the contrary, can be used to induce disentanglement, or at least to minimize annealing and reentanglement.<sup>1,2</sup>

The results of this investigation provide some useful information about laboratory procedures that can be employed to anticipate performance in large scale melt processing equipment. They also provide some insights into the influence of temperature and shear history on the entanglement states in polypropylene melts.

## EXPERIMENTAL

Two fiber grade polypropylenes were obtained, with melt flow indices of 3.0 and 12.0 dg/min.<sup>12</sup> Each polymer existed in two different forms, namely, pellets and powder. The powder was as-produced, directly from the polymerizer, while the pellets had been melted, extruded, and pelletized by the manufacturer. Molecular weight data for these samples are summarized in Table I. These data were obtained by size exclusion chromatography in trichlorobenzene solutions at 145°C. Details of the molecular weight characterization are given elsewhere.<sup>13</sup>

Thermal stabilizers were added to the polypropylenes in our laboratory. Polymer 1 (3.0 MFI) contained a total of 3900 ppm antioxidant, including 1000 ppm Ionol (butylated hydroxytoluene), 1000 ppm Irganox 1010 (tetrakis[methylene-3-(3',5'-di-*tert*-butyl-4' hydroxyphenyl) propionate] methane) and 1900 ppm Irgafos 168 (2,4-di-*tert*-butylphenylphosphite). Sample 2 (12.0 MFI) contained 1300 ppm Ionol, 1000 ppm Irganox 1010, and 2000 ppm Irgafos 168. As shown below, this level of stabilization protected the polypropylenes quite well during extrusion.

It was necessary to remove air from the powdered samples before characterization of their melt behavior. This was accomplished by compression molding 1.5 mm sheets at 175°C. The polymer was in the press 1–2 min for this operation. Molded plaques were chopped in a Wiley mill. The pellet samples were tumbled blended with powdered stabilizer and then used without further preparation.

TABLE I  
Molecular Weights of Starting Materials<sup>a</sup>

Polymer	Melt flow index	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_z$	SD(N) <sup>b</sup>	SD(W) <sup>b</sup>	SKEW(N) <sup>c</sup>	SKEW(W) <sup>c</sup>
1 Pellets	3.0	41,000	228,000	950,000	87,600	405,700	14.9	22.3
1 Powder	3.0	42,000	231,000	986,000	89,100	417,600	15.3	24.1
1 Processed Powder		38,700	212,500	864,000	82,000	372,100	14.6	20.6
2 Pellets	12.0	27,500	165,000	753,000	61,500	311,500	16.3	23.4
2 Powder	12.0	27,700	166,000	740,000	61,800	308,700	16.0	23.6
2 Processed Powder		26,100	157,100	684,300	58,500	287,800	15.6	20.9

<sup>a</sup> polymer samples for molecular weight measurements taken after powder was compression molded and chopped, prior to extrusion.

<sup>b</sup> SD(N), SD(W) = standard deviations of the number and weight distributions, respectively.

<sup>c</sup> SKEW(N), SKEW(W) = skewness of number and weight distributions, respectively.

Melt flow behavior was studied with a fixed plunger speed mechanically driven capillary viscometer—the Instron rheometer<sup>14</sup>—and a laboratory scale 0.5 in. diameter screw extruder.<sup>3</sup>

In screw extruder experiments flat entry capillary dies were used with diameters of 0.8, 1.1, and 3.2 mm. Length to diameter ( $L/D$ ) ratios of these dies were between 1.5 and 8. Screw dimensions were: diameter 0.5 in., pitch 0.5 in., helix angle 17.66°, length 13.5 in., and compression ratio 3:1.

Extrusion pressure was measured with a plastic melt transducer located 0.75 in. upstream from the capillary entrance. Screw speeds ranged between 5 and 50 rpm. Mass flow rates were obtained by weighing extrudates collected over known times. Volumetric flow rates were calculated from the density of the polypropylene melt<sup>16</sup> at the particular extrusion temperature.

Instron rheometer experiments used flat entry dies with diameters of 1.0 and 2.5 mm and  $L/D$  ratios from 4 to 50. Piston velocities ranged from 0.5 to 20.0 cm min.<sup>-1</sup> Instron extrusion experiments were commenced about 2 min after the barrel was loaded, to minimize the annealing time of the polymer in the rheometer barrel. Loading of the barrel occupied 4–5 min. Extrusion results were not affected by variations in the initial level of polymer melt in the barrel, between 16 and 24 cm above the capillary, nor by a high-to-low or low-to-high sequence of piston speeds. Polypropylene samples were exposed to the extrusion temperature for times between approximately 5 and 40 min, after warm-up, depending on the piston speed in the particular experiment. Equilibrium load cell readings were used in calculations of Instron experiment results.

In both the screw extruder and piston rheometer experiments, extruded round filaments were air quenched and collected in 8–10 cm lengths. After standing at room temperature for at least 24 h, extrudate diameters were measured with a micrometer at points around the circumference about 1 cm from the leading end of the sample. Die swell was calculated as the ratio of the diameters of the extrudate and capillary.

With a given capillary die, the apparent shear stress  $\tau$  is given by the well-known expression:

$$\tau = PR/2L \quad (1)$$

where  $P$  is the measured pressure and  $R$  and  $L$  are the die radius and length, respectively. The corresponding apparent shear rate  $\dot{\gamma}$  is

$$\dot{\gamma} = 4Q/\pi R^3 \quad (2)$$

with  $Q$ , the volumetric flow rate given by

$$Q = m\bar{V}/t \quad (3)$$

where  $\bar{V}$  is the specific volume of the polymer melt at the extrusion temperature and  $t$  is the time to collect mass  $m$  of extrudate from the screw extruder.

The corresponding equation for  $\tau$  for the Instron rheometer measurement is

$$\tau = FD/4A_p L \quad (4)$$

where  $F$  is the force on the plunger in the instrument,  $A_p$  is the cross-sectional area of the plunger, and  $L$  and  $D$  are the capillary length and diameter, respectively. The force is computed from

$$F = lg \quad (5)$$

where  $l$  is the measured load on the plunger and  $g$  is the gravitational acceleration constant.

The apparent shear rate in this case is given by

$$\dot{\gamma} = \frac{2}{15} \left( \frac{V_{xh} \cdot d_p^2}{D^3} \right) \quad (6)$$

where  $V_{xh}$  is the vertical speed of the Instron crosshead (in./min),  $d_p$  is the plunger diameter (in.), and  $D$  is the capillary diameter (in.).<sup>18</sup> Replicate screw extruder and Instron flow curves agreed to within better than 5% in all cases.

## RESULTS AND DISCUSSION

Molecular weight data summarized in Table I show that pelletization has affected little change in the molecular weight distributions of these propylene homopolymers. There may have been some narrowing of the molecular weight distribution of the lower melt flow polymer (sample 1), by loss primarily of high molecular weight species. The difference observed between the powder and pelletized versions of this polymer are within the experimental uncertainty of the analysis, however.

When the powder was prepared for extrusion by compression molding and chopping there was some reduction in molecular weight. The data in Table I show that the powder samples *as tested* had slightly lower molecular weights than their pelletized counterparts. As shown below, melts produced from powder samples may nevertheless be more viscous and elastic than those from pellets.

Figure 1 plots apparent shear stress vs. apparent shear rate for polypropylene 1, at 190°C with two different capillaries in the screw extruder. As expected, the die with larger  $L/D$  ratio produces a lower apparent shear stress at given apparent shear rate. With both dies, however, the powder sample is considerably more viscous than the pelletized version. These differences are more pronounced at higher than at lower shear rates. At 1000  $s^{-1}$  in the  $L/D = 3.0$  die the apparent viscosity of the powder is more than double that of the pellets, despite the slightly lower molecular weight of the two compression molded powder version.

These results are consistent with the existence of a higher entanglement density in the powder version of this polymer. The lower melt elasticity of the pellets was apparently induced in passage through the pelletizing extruder during the manufacturing operation. Such effects are expected to

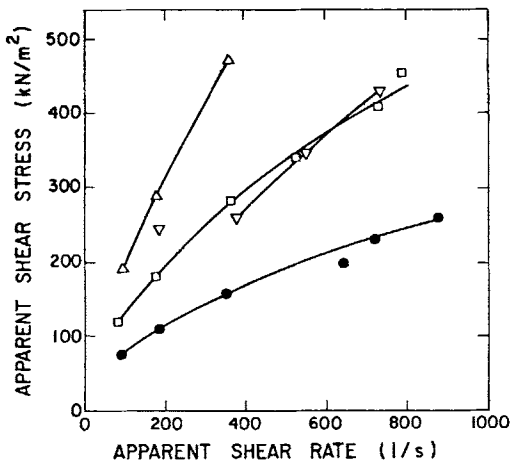


Fig. 1. Apparent shear stress–apparent shear rate plots for polymer 1 pellets (□, ●) and powder (△, ▽) in screw extruder at 190°C. Die diameter was 1.1 mm. The  $L/D$  ratios of the two capillaries used: (△, □) 1.5; (▽, ●) 3.0.

be greater than the extruder is required to melt as well as pump the polymer,<sup>2,5</sup> as with polypropylene, than when the pelletizing unit is melt fed (e.g., in production of high pressure low density polyethylene).

Instron rheometer data presented below show that the various versions of this polymer revert to the same rheological state on annealing in the melt. This entanglement process is quite rapid in this case, compared to that of, say, low melt index low density polyethylene.<sup>4-6</sup> The slower transit time through the extruder at lower shear rates would permit more entanglement than extrusion at higher shear rates. Thus, the powder and pellets differ most from each at the fastest screw speeds and higher apparent shear rates in the die.

Figure 2 shows a similar plot for the same powder and pellet samples on

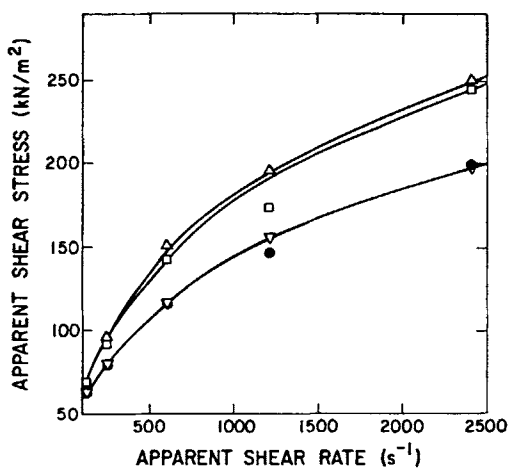


Fig. 2. Apparent shear stress–apparent shear rate plots for sample 1 pellets (□, ●) and powder (△, ▽) in Instron rheometer at 190°C. Die diameter was 1 mm; die  $L/D$  ratios: (△, □) 10; (▽, ●) 15.

the Instron rheometer. Note that in this case the  $L/D$  ratios of the dies are larger than in screw extruder experiments. With the  $L/D_{15}$  die the apparent flow curves for the powder and pellets coincide. The difference between the two is also trivial for the shorter,  $L/D = 10$ , die. The coincidence of flow curves in the Instron experiments results from annealing of the polymer melts when the material is in the rheometer reservoir. Transit times through the Instron apparatus are considerably longer than through the screw extruder.

Screw extruder die swell measurements on polymer 1 are summarized in Figure 3. It is clear that the powder samples have much higher extrudate swell than the pelletized versions. As is normal, die swell increases with apparent shear rate and decreases with increased die  $L/D$  ratio. Instron rheometer die swells for the same polymer are shown in Figure 4. Here the differences between the two samples are almost trivial, except at the highest shear rates used. In this case, the pellet versions have equal or slightly less melt elastic character than the powder samples. The standard deviation of replicate die swell measurements was  $<0.04$ , in all cases.

The die swell observed is consistent with the differences noted earlier in apparent flow curves and the similarities of molecular weights (Table I). The powder samples are more entangled and therefore more viscous and elastic than melts produced from pellets. The annealing effects in the Instron rheometer reservoir tend to reduce these differences compared to the effects seen in screw extrusion. Consistent also is the observation that samples with the same apparent viscosity may still differ in melt elasticity (cf. Fig. 2 and 4). This accords with observations and explanations offered in earlier work with linear polyethylene.<sup>3</sup>

The effects of sample history noted with polymer 1 would be expected to be less pronounced with the lower molecular weight polypropylene 2. Screw extruder apparent flow curves for the lower molecular weight material, sample 2, at 190°C, are given in Figure 5. Conditions are similar to those recorded in Figure 1, for sample 1. The differences between sample 2 powder

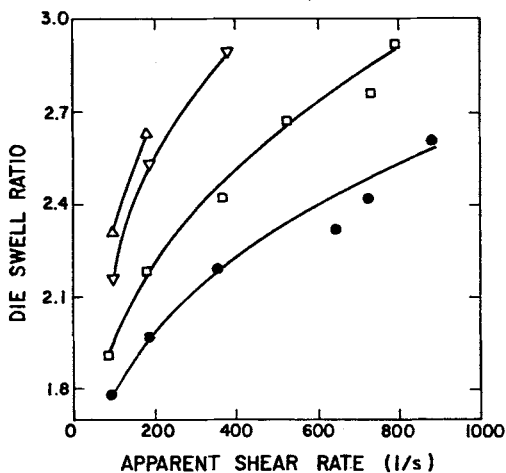


Fig. 3. Die swell ratios for polymer 1 pellets ( $\square$ ,  $\bullet$ ) and powder ( $\triangle$ ,  $\nabla$ ) during screw extrusion at 190°C. Die diameter was 1.1 mm. Capillary  $L/D$  ratios: ( $\triangle$ ,  $\square$ ) 1.5; ( $\nabla$ ,  $\bullet$ ) 3.0.

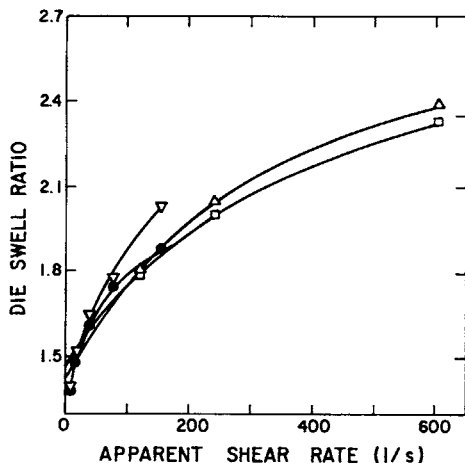


Fig. 4. Die swell ratios for polymer 1 during Instron rheometer extrusion at 190°C: (□) pellets, die  $D = 1$  mm,  $L/D = 15$ ; (△) powder, die  $D = 1$  mm,  $L/D = 15$ ; (●) pellets, die  $D = 2.5$  mm,  $L/D = 8$ ; (▽) powder, die  $D = 2.5$  mm,  $L/D = 8$ .

and pellets are trivial, however, compared to the marked distinctions in the behavior of the two samples of polymer 1.

The differences between sample 2 powder and pellets are somewhat larger in screw extrusion at 175°C, as shown in Figure 6. Here, as in all previous data, the powder is more viscous than the pellets, and this difference is greater at higher shear rates. Recall that the results in Table I show that the powder sample does not have the higher molecular weight.

Higher shear rates were attainable at faster screw speeds in extrusion with pellets than with chopped plaques that were molded from powder. This is because the more uniform shapes of the pellets provided a higher bulk density and better feeding to the screw. The mass output per screw revolution was higher with the pellet feed for this reason.

The variations in extrusion rate at given screw speed are not reflected

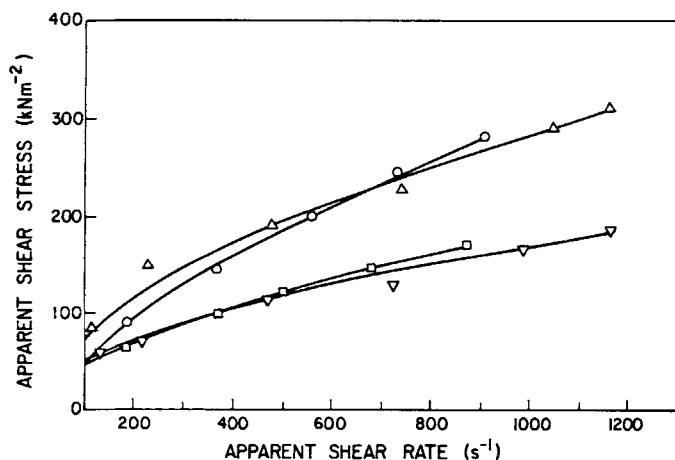


Fig. 5. Apparent flow curves for sample 2 pellets (△, ▽) and powder (○, □) in screw extruder at 190°C. Die diameter was 1.1 mm; capillary  $L/D$  ratios: (○, △) 1.5; (□, ▽) 3.0.



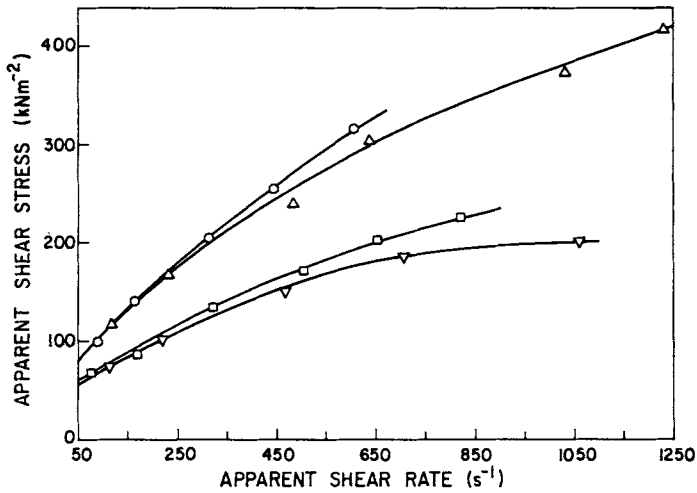


Fig. 6. Apparent flow curves for sample 2 pellets ( $\Delta$ ,  $\nabla$ ) and powder ( $\circ$ ,  $\square$ ) in screw extruder at 175°C. The capillaries are the same as those in preceding figures.  $L/D$ : ( $\circ$ ,  $\Delta$ ) 1.5; ( $\square$ ,  $\nabla$ ) 3.0.

in the apparent flow curves recorded here. A higher mass flow rate resulting from better granule feed will result in a higher head pressure and observed  $\tau$  at the die. Further, the data for polymer 2 (Fig. 5) show little difference in apparent viscosities of powder and pelletizer versions. Polymer 1 exhibited substantial differences (Fig. 1), although the powder and pellet feeds had the same shapes as in polymer 2.

Apparent flow curves from Instron rheometer measurements with polypropylene 2 are shown in Figure 7. Capillaries with very long  $L/D$  ratios were used in these trials because steady extrusion pressures could not be obtained under these conditions with shorter dies with the same diameter. Appreciable load drops were invariably observed with shorter  $L/D$  dies,

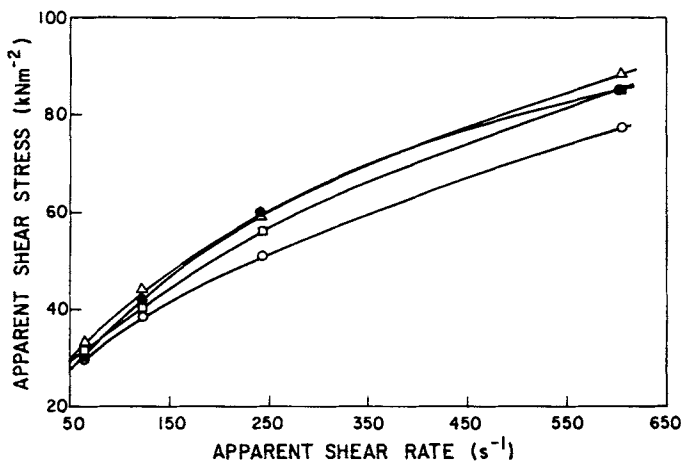


Fig. 7. Apparent flow curves for polymer 2 pellets and powder in Instron rheometer extrusion at 175°C: ( $\circ$ ) pellets, die  $L/D = 40$ ; ( $\square$ ) powder, die  $L/D = 40$ ; ( $\Delta$ ) pellets, die  $L/D = 50$ ; ( $\bullet$ ) powder, die  $L/D = 50$ .

despite efforts to obtain equilibrium values by packing the barrel with more polymer and by applying an excess load before the desired plunger speed was attained.<sup>19</sup>

With an  $L/D$  50 capillary the apparent flow curves of sample 2 powder and pellets coincide. A difference is seen with an  $L/D$  40 capillary, but the distinction is barely greater than the experimental uncertainty in this case. Here also, however, the pelletized sample had a slightly lower apparent viscosity than the powder sample.

Die swell-apparent shear rate plots for polypropylene 2 are shown at 190 and 175°C in Figures 8 and 9, respectively. Although apparent flow curves at 190°C were the same for the powder and pellets, the die swell values differ, with the pellets exhibiting lower melt elasticity. As mentioned, behavior of this type has been seen for high density<sup>3</sup> and linear low density polyethylenes.<sup>2</sup> It reflects the assumption that melt elasticity requires the existence of polymer chains that are entangled with their neighbors at at least two points whereas melt viscosity can be influenced also by the molecules that interact only once along their lengths.<sup>3</sup>

Corresponding die swell results for Instron rheometer extrusions at 175°C with long dies are given in Figure 10. Here there is no difference between powder and pellets with an  $L/D = 50$  capillary. The pellets have slightly lower die swell than the powder in an  $L/D = 40$  die, where the transit time and opportunity for entanglement are less.

Since polypropylene is known to have limited thermal stability, it was of interest also to examine molecular weight distributions of samples that had been through rheological characterization experiments. Results are shown in Table II.

Despite the relatively high level of stabilization of the polymer samples extrusion caused some decrease of molecular weight and a narrowing of the molecular weight distribution. Comparison of pelletized and powdered versions of polymer 1 after extrusion at the same screw speed shows, however, that the molecular weight of the pellet samples was at least as high as that of the powder, despite the lower apparent viscosity and melt elasticity of the pellets.

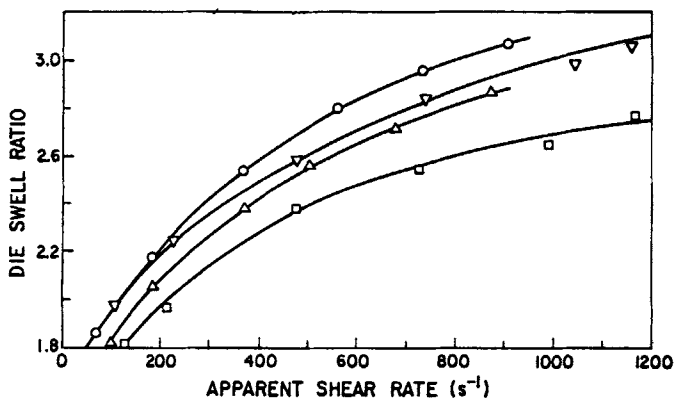


Fig. 8. Die swell values for polymer 2 pellets ( $\nabla$ ,  $\square$ ) and powder ( $\circ$ ,  $\triangle$ ) during screw extrusion at 190°C. Die diameter is 1.1 mm;  $L/D$  ratios: ( $\circ$ ,  $\nabla$ ) 1.5; ( $\triangle$ ,  $\square$ ) 3.0.

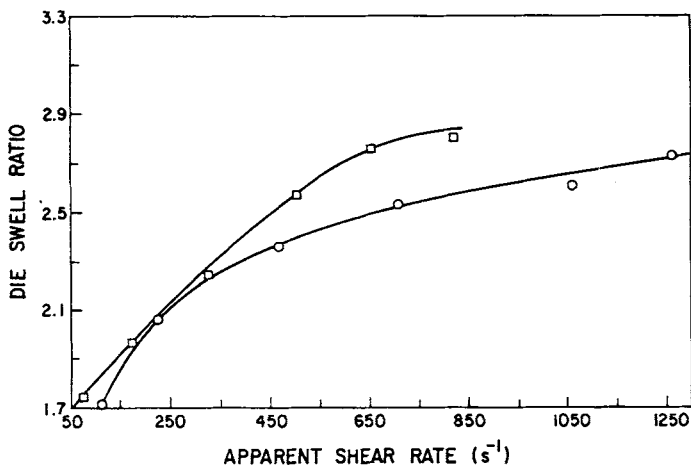


Fig. 9. Screw extrusion die swell values for polymer 2 at 175°C. Die diameter was 1.1 mm and  $L/D = 3$ : ( $\square$ ) powder; ( $\circ$ ) NIBS.

### CONCLUSIONS

The apparent viscosity and melt elasticity of isotactic polypropylene may depend very strongly on the shear and thermal history of the sample. Melt processing of this polymer results in some decrease of molecular weight and change of the initial molecular weight distribution toward a more random character. Nevertheless, pronounced differences may be observed between rheological properties of samples of a polypropylene with the same molecular weight distribution but different melt histories.

Such differences are more likely to be observed the higher the polymer molecular weight. These property changes are attributable to differences in entanglement density. Shearing in the melt causes a reversible disentanglement, resulting in lower melt elasticity and apparent viscosity.<sup>1,3,5</sup>

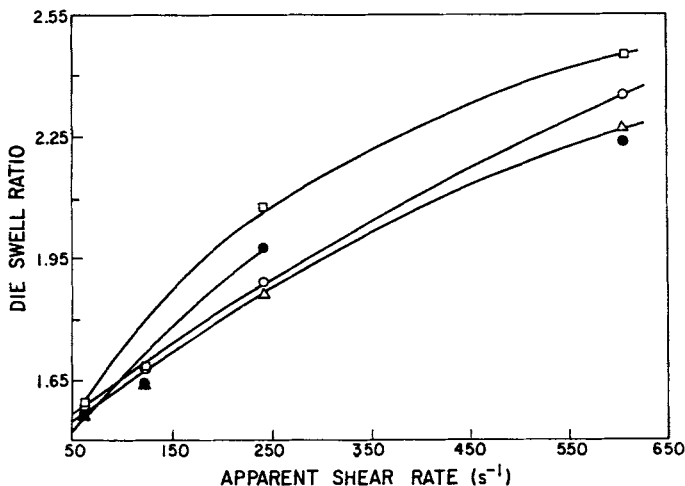


Fig. 10. Die swell values for polymer 2 during Instron rheometer extrusion at 175°C. Capillary diameter = 1 mm: ( $\circ$ ) pellets,  $L/D = 40$ ; ( $\square$ ) powder,  $L/D = 40$ ; ( $\triangle$ ) pellets,  $L/D = 50$ ; ( $\bullet$ ) powder,  $L/D = 50$ .

TABLE II  
Molecular Weights of Extruded Polypropylenes

Polymer	Rheological history	Screw speed (rpm)	Temp (°C)	Shear rate (s <sup>-1</sup> )	Polymer characteristics				
					$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_z$	SD(W)	SKEW(W)
1 Pellets	Starting material	—	—	—	41,000	228,000	950,000	405,700	22.3
1 Pellets	Screw extruder	10	190	305	39,800	221,700	930,000	396,300	21.9
1 Pellets	Screw extruder	30	190	910	37,300	207,300	898,000	378,400	20.1
1 Pellets	Screw extruder	50	190	1360	33,500	173,700	798,500	329,400	19.4
1 Powder	Starting material	—	—	—	38,700	212,500	864,000	372,100	20.6
1 Powder	Screw extruder	10	190	180	37,300	205,700	910,500	380,800	21.2
		30	190	500	35,700	196,300	897,000	370,900	21.1
		50	190	790	32,300	169,500	792,000	324,800	19.8

Annealing of polypropylene in the melt promotes molecular entanglement and tends to erase differences caused by shear and thermal history variations. For this reason, rheological characterizations in screw extruders may produce different results from the behavior of the same polymers in capillary rheometers, where the polymer experiences very little mechanical shear and prolonged static storage at melt temperatures.

The results reported here should be of interest to polymer manufacturers for several reasons. They indicate that rheological characterization methods should be designed to match subsequent processing operations. Misleading conclusions may be obtained in some cases if the polymer is annealed more effectively in laboratory than factory processes. The data of this article also show that the balance of properties of a polymer may be affected by post-polymerization operations, which must be controlled in order to provide polymers with consistent properties.

Rheological data are notorious for their poor precision. A major factor in this lack of reproducibility may be uncontrolled entanglement density variations.<sup>1,20</sup>

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### References

1. A. Rudin and H. P. Schreiber, *Polym. Eng. Sci.*, **23**, 422 (1983).
2. J. W. Teh, A. Rudin, and H. P. Schreiber, *Plast. Rubber Processing Appl (London)*, **4**, 157 (1984).
3. H. P. Schrieber, A. Rudin, and E. B. Bagley, *J. Appl. Polym. Sci.*, **9**, 887 (1965).
4. M. Rokudai, *J. Appl. Polym. Sci.*, **23**, 463 (1979).
5. J. W. Teh, A. Rudin, and H. P. Schreiber, *J. Appl. Polym. Sci.*, (1984), to appear.
6. T. Fujiki, *J. Appl. Polym. Sci.*, **15**, 47 (1971).
7. F. C. Stehling, C. S. Speed, and L. Westerman, *Macromolecules*, **14**, 698 (1981).
8. J. H. Prichard and K. F. Wissbrun, *J. Appl. Polym. Sci.*, **13**, 233 (1969).
9. A. Rudin, *Soc. Plast. Eng. J.*, **26**, 58 (1970).
10. H. A. Pohl and C. G. Gogos, *J. Appl. Polym. Sci.*, **5**, 67 (1961).
11. K. Kamide and K. Fuji, *Kobunshi Kagaku*, **24**(262), 120 (1967); *Chem. Abstr.*, **68**, 30102f (1968).
12. ASTM D-1238-79, American Society for Testing of Materials, Philadelphia, 1982.
13. V. Grinshpun and A. Rudin, *J. Appl. Polym. Sci.*, (1984), to appear.
14. E. H. Merz and R. E. Colwell, *Am. Soc. Testing Mat. Bull.*, (232), **63**, (1958).
15. J. W. Teh, A. Rudin, and H. P. Schreiber, *Plast. Rubber Processing Appl (London)*, **4**, 157 (1984).
16. S Newman, *J. Polym. Sci.*, **47**, 111 (1960).
17. A. Rudin, *The Elements of Polymer Science and Engineering*, Academic, New York, 1982.
18. Operating and Maintenance Instructions, Instron Capillary Rheometer Type MCR, Instron Corporation, 1965.
19. A. Rudin and H. P. Schreiber, *J. Polym. Sci.*, **44**, 261 (1960); *J. Appl. Polym. Sci.*, **3**, 122 (1960).
20. A. Rudin and K. K. Chee, *J. Appl. Polym. Sci.*, **16**, 403 (1972).

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